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Contamination, potential bias and humidity effects on electrical performance and corrosion reliability of electronic devices

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Summary

This paper describes the interactions between flux contamination, humidity and potential bias and their effect on corrosion reliability. Water layer formation on laminate surfaces and behavior of different solder flux chemistries with humid conditions have been studied, together with their influence on electrical performance of electronics. The effect of the type of laminate's solder mask on the formation of water film and droplets was investigated for two different types: smooth glossy and rough matte surface finishes of the solder mask. The impact of potential bias on the electrical response of electronics is estimated as a function of contamination type under cycling humid conditions. The results show the correlation between the ionic contamination type and water layer formation on surfaces in the presence of the flux residue.

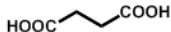


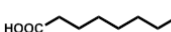
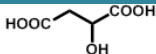

1 Introduction

Electronics industry is using “no-clean” solder flux technology for each kind of soldering process as it is assumed that the residue left after soldering process will be at minimal and non-harmful level. The use of low solid content in “no-clean” fluxes is supposed to lead to its full decomposition/removal after carrying out the soldering step. However, because of many factors influencing flux decomposition [1], in real conditions the printed circuit board assemblies (PCBAs) are being contaminated with significant amounts of active flux residue [2-4]. It is known that the chemical composition of flux applied onto the PCBA surface has an influence on the amount, type and corrosive behaviour of residue compromising the climatic reliability of an electronic device [5] [6].

Typically, “no-clean” solder flux systems consist of: **activators** (organic dicarboxylic acids, halide compounds or combination of both), **solvents** (alcohols, ethers, hydrocarbons, water etc.), **vehicles/binders** (solids, non-volatile liquids or combination of both) and **additives** (surfactants, stabilizers, inhibitors, dyes, plasticizers etc.). Some of the typically found organic flux activators are described in Table 1. In practice, hundreds of flux types exist in the industry, i.e. not only those containing a single-activator but also some mixtures of few different organic species. Because of the complex hygroscopic chemistry and reactions taking place at high soldering temperatures, it is not easy to estimate the corrosive effect of such flux systems on electronic device. In a humid environment water from the surrounding air will be attracted by such residues and cause dissolution of the hygroscopic flux compo-

nents that will lead to the formation of a conductive medium which will carry electrical current (leakage current). This can cause malfunctioning of the electronic device. Entering the electrochemical reactions like corrosion which is likely to take place on PCBA [7-13] is then very easy.

Table 1. Organic acids typically found in solder flux systems – summary of physical and chemical properties taken from Reaxys Chemical Database and Toxicology Data Network (U.S. National Library of Medicine). Except where noted otherwise, data is given for materials in their standard state.

| WEAK ORGANIC ACIDS (WOAs) |  |  |  |  |
|--|---|---|--|---|
| | Succinic acid | Glutaric acid | Adipic acid | Suberic acid |
| Name | Succinic acid | Glutaric acid | Adipic acid | Suberic acid |
| Molecular formula | C ₄ H ₆ O ₄ | C ₅ H ₈ O ₄ | C ₆ H ₁₀ O ₄ | C ₈ H ₁₄ O ₄ |
| Molar mass | 118,09 g/mol | 132,12 g/mol | 146,14 g/mol | 174,2 g/mol |
| Melting point | 185-189°C | 95-98°C | 151-154°C | 140-144°C |
| Boiling point | 235°C | 302-304°C | 337°C | 345.5°C |
| pK_{a1} ; pK_{a2} | 4.21 ; 5.65 | 4.34 ; 5.3 | 4.44 ; 5.43 | 4.52 ; 5.33 |
| Solubility in H₂O | 83,5 g/L [1] | 1400 g/L [1] | 24 g/L [1] | 11,9 g/L |
| |  | |  | |
| Name | DL-Malic acid | | Palmitic acid | |
| Molecular formula | C ₄ H ₆ O ₅ | | C ₁₆ H ₃₂ O ₂ | |
| Molar mass | 134,09 g/mol | | 256,42 g/mol | |
| Melting point | 130-132°C | | 61-63°C | |
| Boiling point | 150°C (decomposition) | | 351-352°C | |
| pK_{a1} ; pK_{a2} | 3.4 ; 5.2 | | 4.78 ; - | |
| Solubility in H₂O | 1400 g/L _{26°C} [1] | | 0,00072 g/L _{20°C} [1] ; 0,00004 g/L | |

Although it is generally known that different flux activators have different hygroscopic nature and their presence on the PCBA surface can cause various corrosive problems, no systematic work is reported investigating the effect of flux mixtures on reliability of electronic products. Investigations in this paper aim to show the differences in hygroscopic contamination types and behavior, and compare it with already known single-constituent flux residue.

Moreover, while studying the water formation on surfaces (clean and contaminated), the influence of surface appearance/finish of the laminates has been investigated. To our knowledge, there is no reported study investigating the effect of surface features on the water and contamination behavior in humid conditions. In this study, two extremely different types of laminates' solder masks (smooth glossy and rough matte) were chosen.

2 Materials and methods

2.1 Test chambers

Experiment involving the observation of flux appearance under full condensing conditions was conducted in a plastic air-tight box, filled with cups of deionized water. Experiments were started when humidity level (RH) inside the plastic chamber has reached 60-65%RH. The temperature of the measurement was around $25 \pm 1^\circ\text{C}$.

The electrical measurements involving exposure to controlled humid conditions were performed in the climatic chamber Espec PL-3KPH. The accuracy of temperature and humidity fluctuations are within $\pm 0.3^\circ\text{C}/\pm 2.5\%\text{RH}$ in the range of -40°C to $+100^\circ\text{C}/20\%\text{RH}$ to 98%RH. The highest relative humidity level used in described experiments was above the level of humidity and temperature for which accuracy of the chamber was specified. However, a further increase in actual RH in the chamber with an increase of RH settings for the chamber was verified using humidity sensors.

2.2 Test boards

Water layer formation and flux appearance under fully condensing conditions were studied using laminate substrates with solder mask of two types of surface finish (Fig. 1): smooth glossy and rough matte. The thickness of the boards was 1.6 mm and the dimensions of the substrates were 1.5 cm x 1.5 cm – 1.9 cm x 1.9 cm.

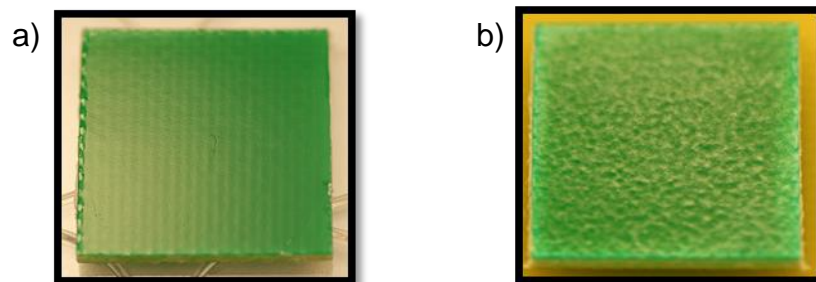


Fig. 1: Laminates with solder mask of: a) smooth glossy finish; b) rough matte finish.

The temperature differences that are likely to be experienced by electronic materials in service life were simulated by decreasing the temperature of the test boards by placing them on an aluminium block with an embedded Peltier element (cooling stage). The heat generated by the other side of Peltier element was dissipated by mounting an aluminium block below it. The 3 – 3,5V voltage was applied by using a DC power supply. The temperature of the laminate materials pasted on the aluminium block was measured with a temperature sensor (PT100 class A). A DaqLink data logger “Fourier Systems DBSA710” was used to measure the temperature of a surface during the experiment. With the use of DinoLite video microscope it was possible to in situ monitor the effect of temperature change and different contamination on water layer formation on various surfaces.

All electrical measurements were conducted with the use of SIR comb pattern (Surface Insulation Resistance) with a HASL finish (hot air solder leveled - Sn/Ag/Cu solder alloy), on the FR-4 test board. The dimension of the pattern is 13 × 25 mm, and the pitch spacing size of 0.3 mm.

All the test boards were carefully cleaned prior to the testing. Initial rinsing with ultrapure Millipore water for approx. 30 seconds (resistivity of 18.5-20.5 MΩ at 25°C) was followed by rinsing with isopropyl alcohol for approx. 60 seconds (analytical purity of 99.8%) and drying with pressurized air.

2.3 Contaminants

For the observation of water absorption by different solder flux contaminants in condensing conditions, four Weak Organic Acids (WOAs) were chosen: adipic, succinic, glutaric and DL-malic. Additionally, four commercially available “no-clean” solder flux systems were chosen (Table 2) to study the effect of activators’ mixtures on water absorption from surrounding environment. The contaminants were applied onto two different laminate materials in the amount range of 0,25-0,5 μg over 5-12,5 mm^2 . Table 2 summarizes the information about flux classification according to J-STD-004 ranking standard, the type of activator (obtained from Safety Data Sheets, Fourier Transform Infrared Spectroscopy or Ion Chromatography analysis), acid number and solid content. All of them are liquid-type volatile organic compounds- (VOC-) or water-based fluxes used for wave or selective soldering process. The overall and specific composition of the fluxes is confidential.

Table 2: Commercial no-clean flux systems and their characteristics.

| Flux symbol | Acidic constituent (activator) | J-STD-004 standard designation* | Acid value [mg KOH/g] | Solid content [% wt] |
|-------------|------------------------------------|---------------------------------|-----------------------|----------------------|
| SF1 | Succinic + adipic acids | ORL0 | 26 | 4 |
| SF2 | Glutaric + adipic acids | ORM0 | 37 | 4 |
| SF3 | Glutaric + succinic + adipic acids | ORL0 | 32 | 4 |
| SF4 | Succinic + rosin acids | ROL0 | 20 | 5 |

*First two letters specify the filmformer type: **RO**-rosin, **OR**-organic; third letter specifies the level of activator in the flux: **L**-low, **M**-medium; the last number specifies halides content: **0**-(<0.05% wt/wt).

Impedance measurements were performed in order to understand the influence of different flux chemistry and temperature on water uptake and resulting electrical response from the system. The test boards with SIR patterns were cleaned and pre-contaminated with four WOAs (adipic, succinic, glutaric and DL-malic acids) dissolved in isopropyl alcohol prior to application onto the comb patterns by automatic pipette. The contamination level was $\sim 100 \mu\text{g}/\text{cm}^2$.

2.4 Impedance measurement

Impedance measurements were performed with the use of “BioLogic VSP” multichannel potentiostat. The change of impedance of the water layer formed on the SIR pattern as a function of different contamination type, humidity and temperature was measured for one cycle of humidity ramp up and down (ramp rate: 1%RH/2 min). The signal amplitude of 25 mV ($V_{\text{rms}} = 17.68 \text{ mV}$) in the frequency of 1 kHz was applied. The contaminants tested were four WOAs and four flux systems. Testing temperatures were $25 \pm 1^\circ\text{C}$ (all) and $40 \pm 1^\circ\text{C}$ (except for SF3).

3 Results and discussion

3.1 Water layer formation on clean laminates

Two samples of laminates were chosen (Fig. 1) for investigating the water layer formation differences and the dependency of the solder mask surface finish. The substrates were mounted to the Peltier cooling element with heat transfer paste and closed in an air-tight box filled with water cups. The temperature inside this chamber was around $25 \pm 1^\circ\text{C}$, and after around 20 minutes the humidity level reached around 60-70%RH. At this point the measurement started and the photographs were in situ recorded (Fig. 2 and 3) showing the water film and droplets formation as the temperature of both materials was being reduced.

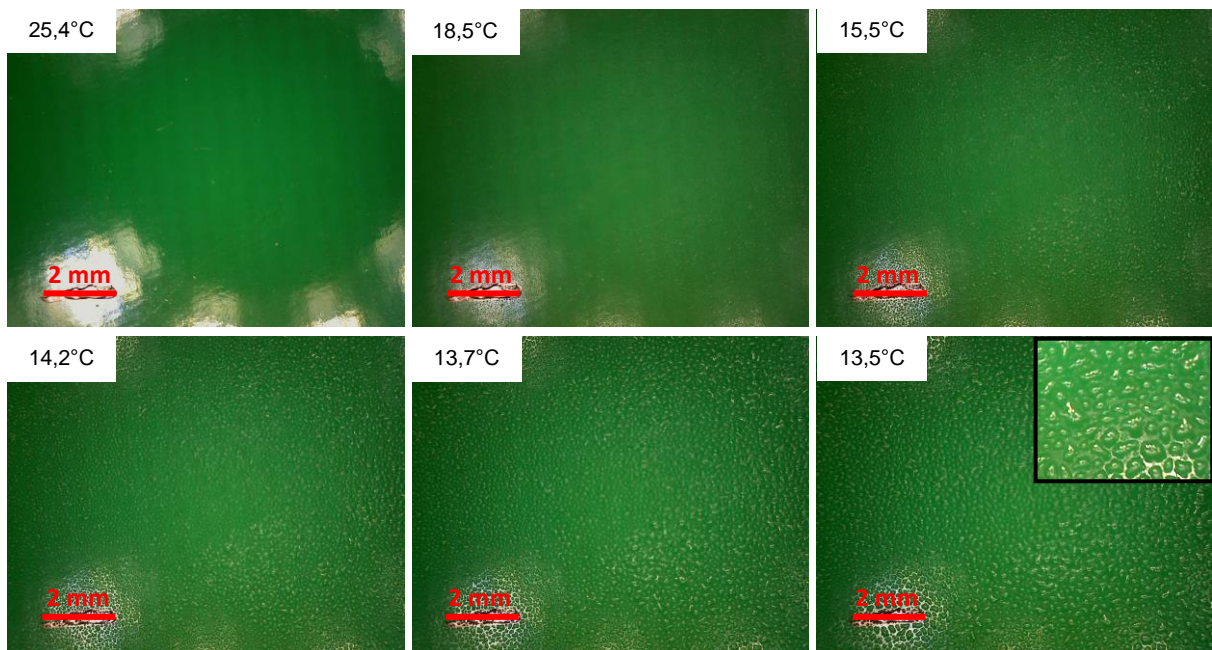


Fig. 2: Water film and droplets formation on smooth glossy surface finish of solder mask.

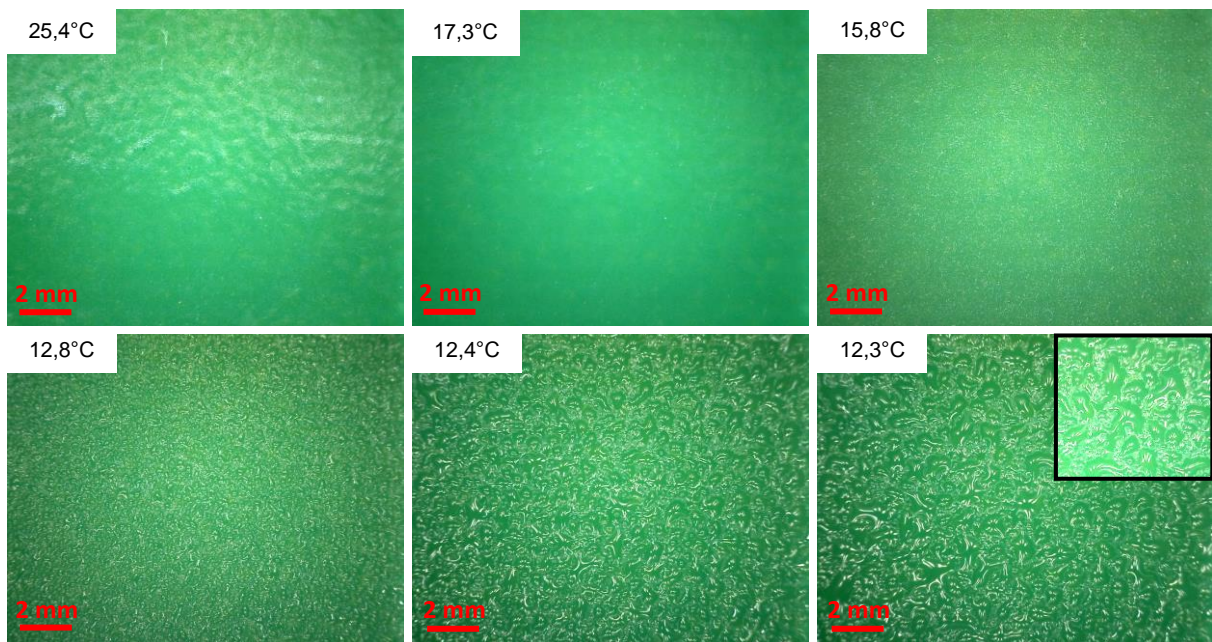


Fig. 3: Water film and droplets formation on rough matte surface finish of solder mask.

After the point when temperature of laminate's surface goes below 18°C, the water film can be seen to form in case of both substrates. With the subsequent decrease of temperature, more and more droplets are being formed, reaching the point where they start to connect one to another. On the smooth glossy type of solder mask, the initial formation of water layer (observed as reflection of camera light gets poorer) seems to be rather uniform. An uptake of higher water amounts result in formation of bigger, rather concentric droplets, not spreading over laminate area. However, in the case of rough matte solder mask, there seem to exist some preferable areas where water droplets form faster than on other areas. This is possibly the effect of trapping firstly formed droplets in the voids of solder mask structure. Water droplets formed under such condensing conditions have rather random, non-defined shape, and are more likely to spread on the surface to connect with other droplets, on the contrary to their behaviour on smooth glossy solder mask. This suggests the different surface energies for both materials which highly influences wetting of water droplets and subsequent possible spreading of contamination.

3.2 Water layer formation on contaminated laminates

The influence of different pure flux activators on water uptake in condensing conditions was investigated with the use of previously tested (par. 3.1) different laminates. The contaminated substrates (Fig. 4 and 5) were placed in a box with 60-70%RH and cooled down to visualize the differences in water formation on contaminated areas.

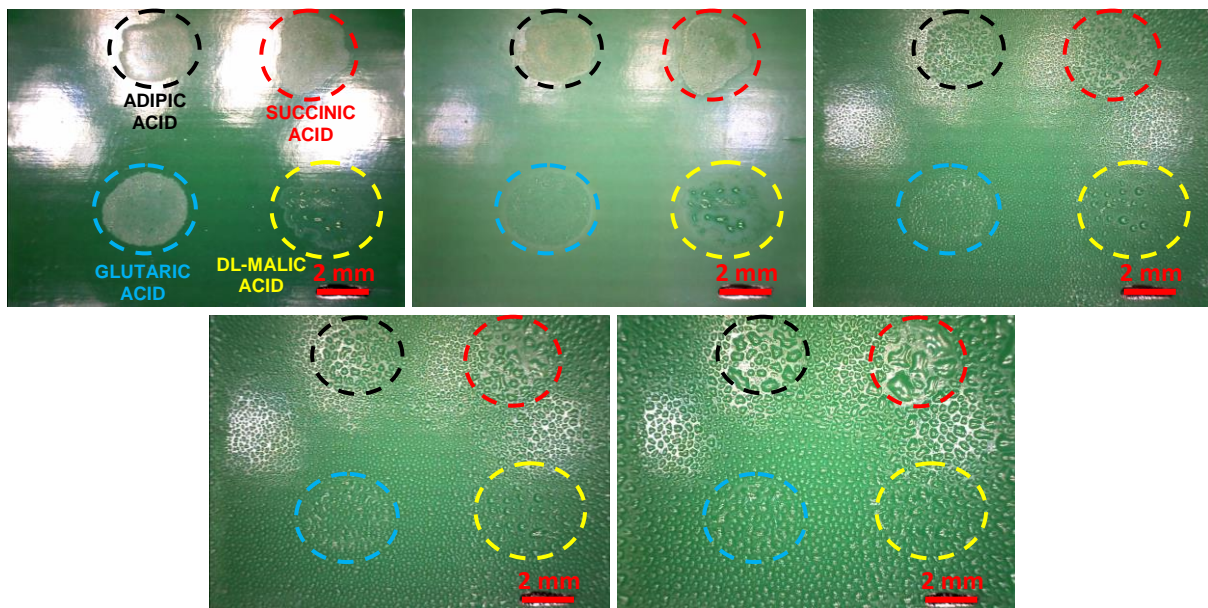


Fig. 4: Water absorption by different flux activators contaminating smooth glossy solder mask.

It can be clearly seen that in case of rough solder mask, the effect of water uptake in condensing environment is higher than in the case of smooth laminate. DL-Malic and succinic acids attract more water than adipic and glutaric acids, forming bigger droplets of saturated solutions. Such strong effect is not observed for smooth glossy surface finish, despite of the same residue amount applied, and cooling both substrates in the same rate for the same time of measurement. Among tested acids, DL-malic, glutaric and succinic have higher solubility and are more hygroscopic than adipic. Hence, attraction of water molecules will be higher for those three activators. However, as proved here, water uptake seems to be different for the same acid tested on

two different surfaces. Similar effect of differences in surface energy was shown in par. 3.1.

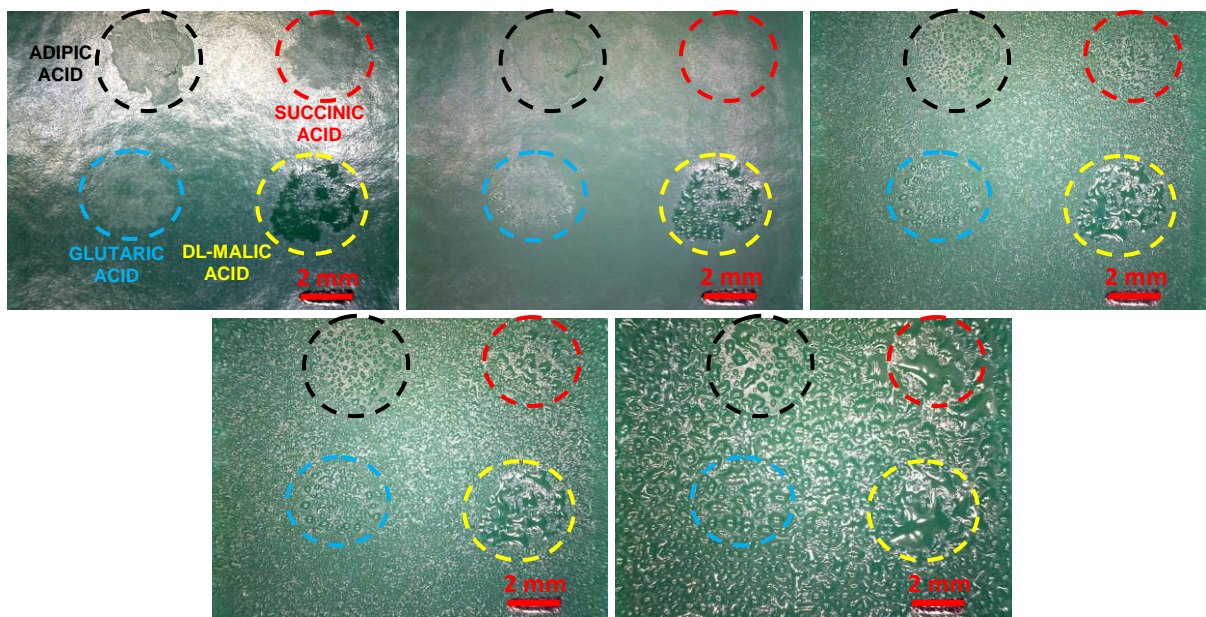


Fig. 5: Water absorption by different flux activators contaminating rough matte solder mask.

Four typical flux systems containing blends of two or three organic activators were tested in condensing conditions in the same way as pure flux activators (Fig. 6 and 7).

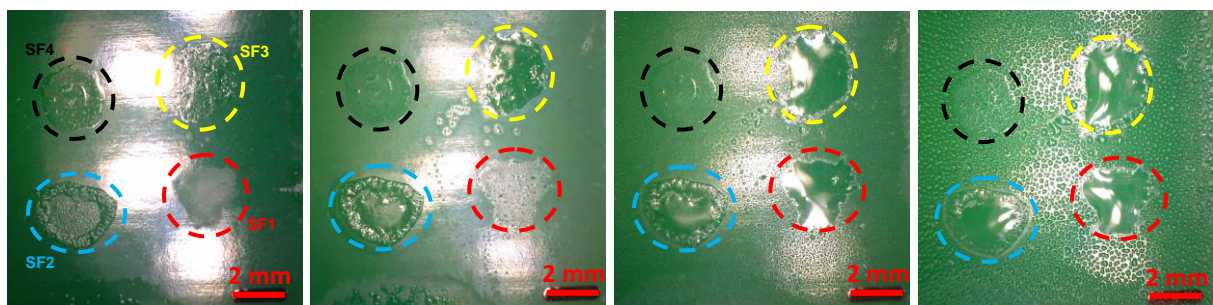


Fig. 6: Water absorption by different fluxes containing activators' mixtures contaminating glossy solder mask.

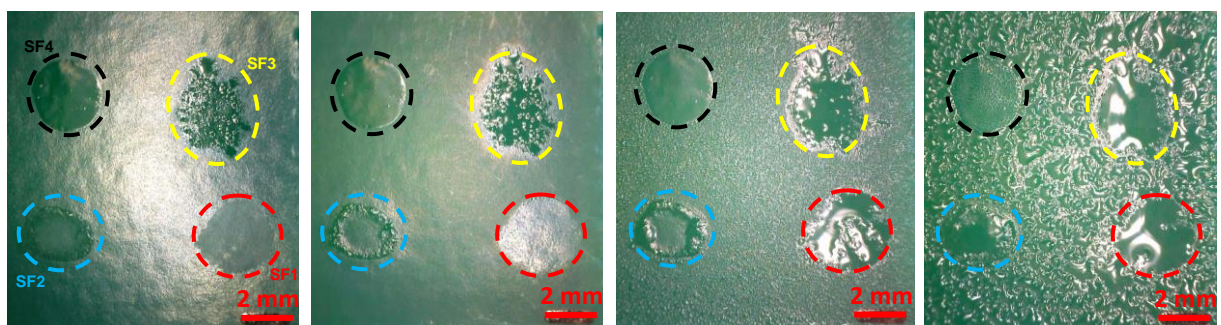


Fig. 7: Water absorption by different fluxes containing activators' mixtures contaminating rough matte solder mask.

These fluxes contain mixtures of activators: succinic + adipic (SF1), glutaric + adipic (SF2), succinic + glutaric + adipic (SF3) and succinic + rosin acid (SF4). In comparison to single contaminants, three (SF1-3) out of four tested fluxes attract more water than their single constituents do alone. Only the rosin containing flux formed rather

hydrophobic film on the surfaces, not allowing big droplets of water to be formed. The water uptake by three other fluxes seems to be rather similar for both types of solder masks, although flux containing the mixture of three organic acids (SF4) is spreading over rough laminate surface more easily, getting outside of initial contamination area.

Out of all flux contaminants tested, those containing mixtures of activators seem to absorb more water than their separate single components. This could be due to the fact that in mixtures, the deliquescence point is shifted towards lower humidity values in respect to the deliquescence point of single components of the blend [14].

3.3 Impedance measurement

Investigation of the effect of different WOAs and flux mixtures on the electrical signal as a function of RH and temperature was tested using AC Impedance Spectroscopy. With the humidity ramp up, the initial adsorption of thin water film onto the PCBA surface is followed by subsequent dissolution of contamination and the formation of saturated conductive electrolyte. At the certain humidity level, the impedance values drop down meaning that the substance dissolved into the water layer causing reduction of the electrolyte resistance. Figures 8 and 9 show the impedance spectra of four WOAs and four flux systems, respectively, for the cycle of increasing and decreasing the RH (30~99%RH) at $25 \pm 1^\circ\text{C}$ and $40 \pm 1^\circ\text{C}$ with the ramp rate of 1%RH/2 min.

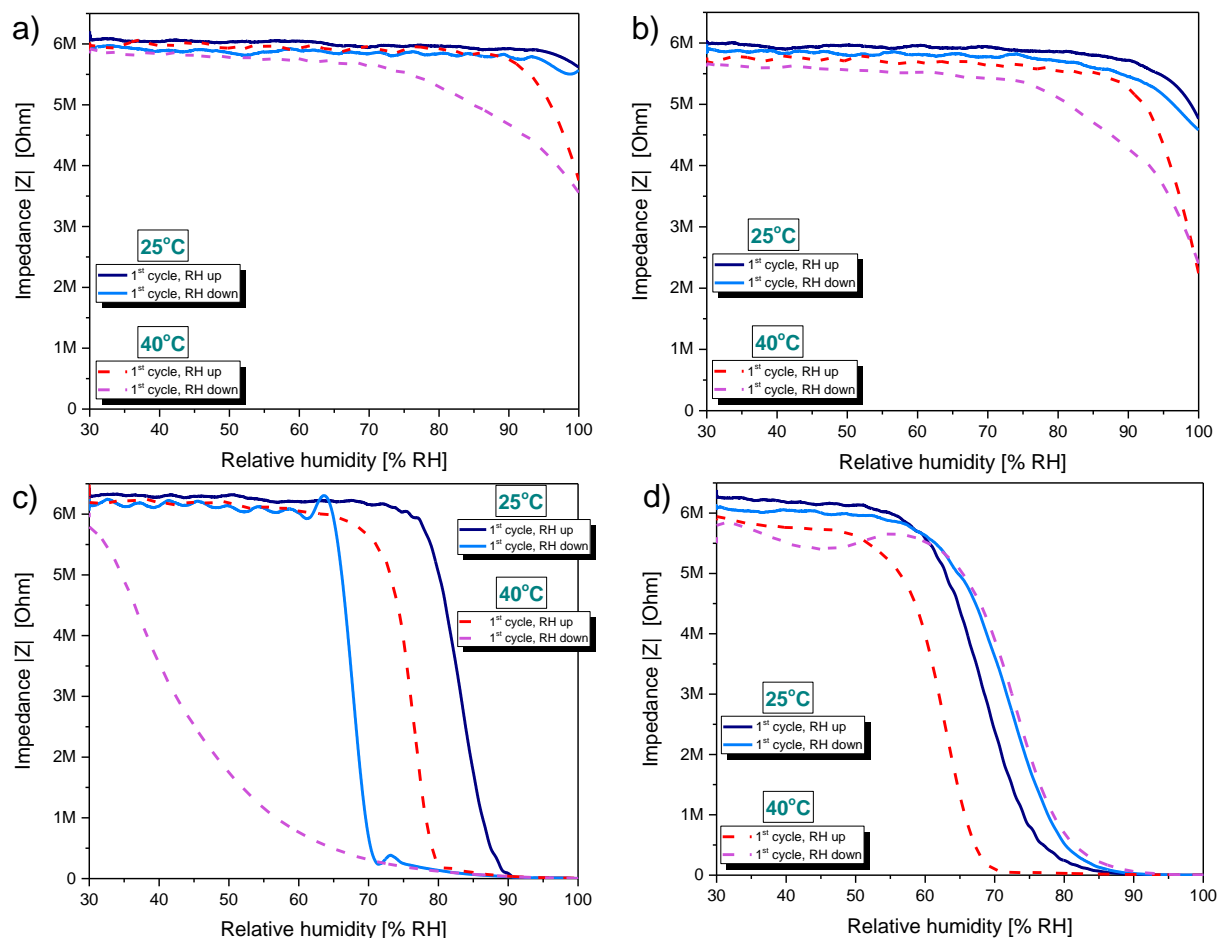


Fig. 8: Impedance spectra for WOAs: a) adipic acid; b) succinic acid; c) glutaric acid; d) DL-malic acid.

Increase of humidity does not affect much the electrical response when testing adipic and succinic acids at 25°C. Only at highest humidity levels, the resistance of water layer formed decreases slightly for succinic acid. However, conducting the same measurement at 40°C, the critical RH (cRH) indicating the formation of conductive solution is shifted towards lower RH values, meaning the decrease of water layer resistance happens faster (at lower RH levels) than at 25°C. For glutaric and DL-malic acids, the cRH at 25°C is shifted more towards lower humidity levels in respect to two previously mentioned acids. Similarly, when increasing the temperature of the test, the rcRH (recrystallization RH) for both acids shifts towards lower RH values.

For all of the impedance spectra, the hysteresis behaviour can be seen, meaning that the recrystallization (when humidity ramps backwards) will take place at lower humidity levels than the deliquescence occurred.

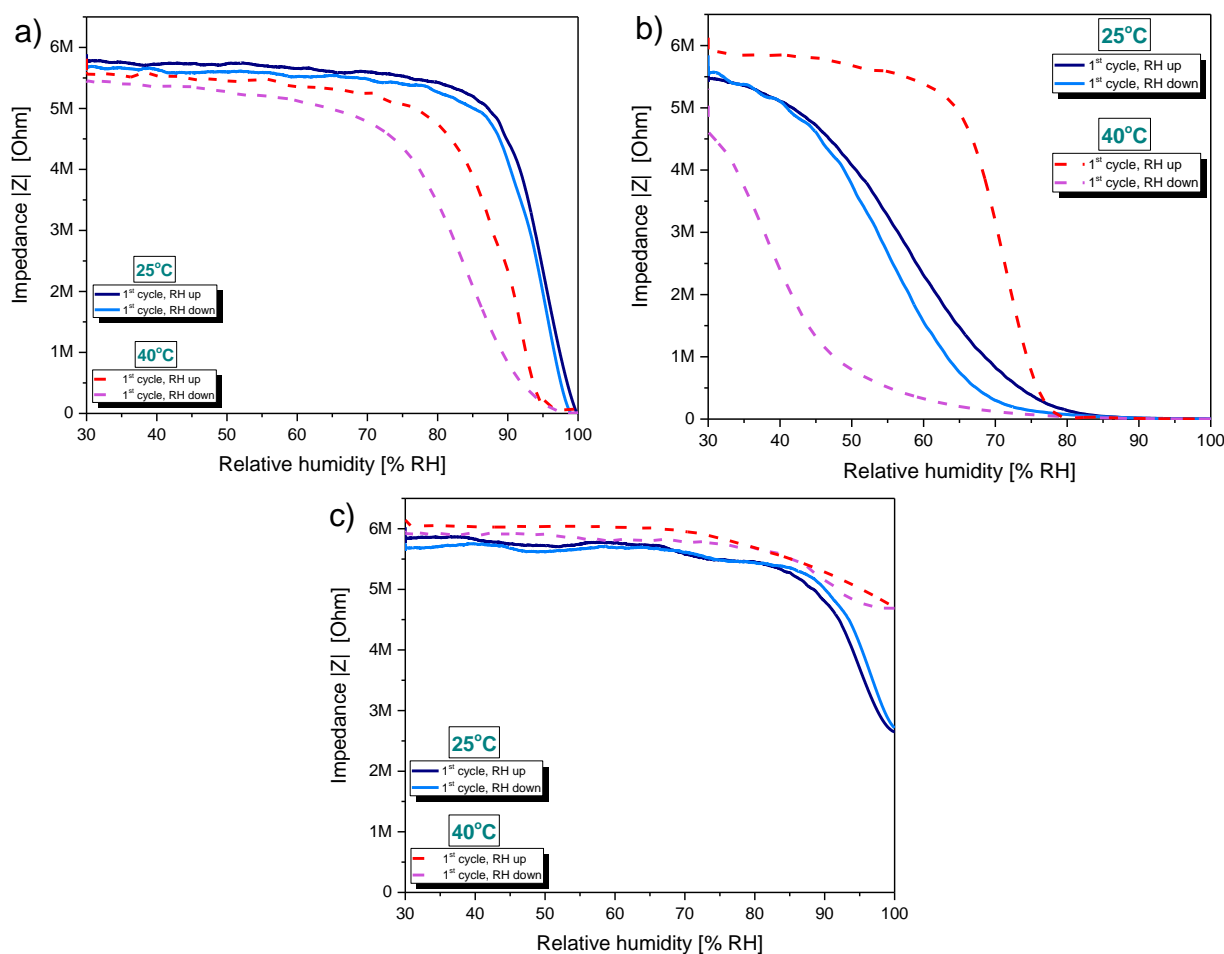


Fig. 9: Impedance spectra for flux systems: a) SF1; b) SF2; c) SF4.

Similar effects can be observed for tested flux systems (Fig. 9). Increase of the temperature of measurement shifts both cRH and rcRH for SF1 (succinic + adipic) towards lower RH values, meaning that at 40°C the absorption of water will take place faster than when it happens at 25°C. For SF2 (glutaric + adipic) only the rcRH is shifted that way but absorption of water seems to take place later than it happens when carrying out the measurement at 25°C. This could be explained by a very fast humidity ramp (1%RH/2 min) which in this case gives an impression that cRH is shifted towards higher humidity levels. For SF4 (succinic + rosin acids) neither significant hysteresis behaviour nor shift of cRH and rcRH are observed. This flux may not have such activating properties as other flux systems tested, as the main component of SF4 is rosin which will not behave as other typical organic activators. Increasing

the measurement temperature does not evolve the small amount of encapsulated succinic acid. For the mixture of SF3 (glutaric + succinic + adipic) it was not possible to obtain reliable impedance spectra as this flux seem to have more hygroscopic properties than any of its constituents. More investigation needs to be done in order to explain the effect of humidity ramp rate on deliquescence and efflorescence of activators blends.

4 Conclusions

- Surface features of solder mask covering laminate materials have an impact on water film formation and wetting of those surfaces. Rough matte surface finish allows water to form droplets of random shape and spread over laminate surface more easily. Smooth glossy solder mask, on the other hand, keeps water droplets of more concentric shape in place, not allowing to spread over the entire surface.
- This effect of surface finish has an impact of spreading the contamination over surfaces in humid conditions. On rough matte solder mask some contamination types are susceptible to take up more water from the surroundings than they do when applied onto smooth surface.
- In blends containing few activating components with deliquescent behavior in the flux, the humidity level of solid dissolution will be shifted towards lower RH values. This means that such mixtures can have more aggressive nature for corrosion of printed circuit boards than their individual constituents.
- For humidity cycling, the hysteresis behaviour of saturation and drying out is observed. Usually, the recrystallization of dissolved contaminant will happen at lower humidity than its dissolution happens.

5 Acknowledgements

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